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PREVENTION OF PINKING IN RUBBER ARTICLES CONTAINING DI-BETA-NAPHTHYL-PARA-PHENYLENE DIAMINE ANTIOXIDANT

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This invention relates to the compounding of rubber in such manner that development of the pink discoloration which results from the presence in the rubber of symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant is prevented.

Symmetrical di-beta-naphthyl-para-phenylene diamine is one of the best all-around anti-oxidants for vulcanized rubber thus far developed. However, it exhibits the objectionable characteristic that it turns pink when it is subjected to certain conditions, particularly when subjected to light and oxidizing conditions. Under ordinary storage conditions pinking does not occur. However, pinking appears to be catalyzed by light, and certain oxidizing media such as nitric oxide fumes and ozone; and where these conditions prevail, pinking often becomes very rapid. Pinking occurs also during bleaching operations, such as with chlorine and hydrogen peroxide, especially the former. This pink discoloration changes the color or shade desired for the article and is highly objectionable.

The problem of pinking as a result of the use of this anti-oxidant in rubber compositions and articles containing the same is particularly serious in the case of light-colored vulcanized rubber compounds, such as those which are cream-colored, blue, yellow, so-called natural, white, etc. The reason is that the development of the pink by decomposition or other change of the anti-oxidant changes the shade from that which is desired.

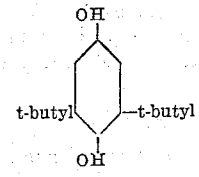
The problem of pinking is especially serious in the case of articles or materials made from or containing elastic yarn comprising a core of vulcanized rubber containing the above anti-oxidant and a wound covering of textile yarn. This problem is particularly serious where white or light-colored textile yarns are used as the covering for the elastic core or in association with the elastic yarn to make the fabric of which the article or material is formed or woven. The pink discoloration which occurs as a result of the above anti-oxidant in the vulcanized rubber core of the elastic yarn usually shows through the associated white or light-colored textile yarns and fibers, often in an irregular or non-uniform manner, and this is highly objectionable.

Elastic yarn of the type just referred to is described in detail in the Adamson Patent 1,822,847. This elastic yarn typically has a core of elastic vulcanized rubber under tension with a covering of a plurality of helical, preferably both right and left, windings which hold

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the core elongated, the yarn having a predetermined capacity to stretch.

I have now made the surprising discovery that the development of pink discoloration in vulcanized rubber articles containing symmetrical di-beta-napthyl-para-phenylene diamine as an anti-oxidant can be prevented by incorporating in the rubber composition, prior to vulcanization, 2,5-di-tertiary butyl hydroquinone. This compound has the structural formula



Although I have found that 2,5-di-tertiary butyl hydroquinone by itself is a poor rubber anti-oxidant, it operates in some manner not understood at present to greatly suppress the normal tendency of symmetrical di-beta-naphthyl-para-phenylene diamine to cause a pink discoloration. This is illustrated by the following examples. In all of the examples, the same basic formulation was used, the only difference being the addition of symmetrical di-beta-naphthyl-para-phenylene diamine alone in Example 1, the use of 2,5-di-tertiary butyl hydroquinone in Example 2 and the use of the two compounds in combination in Examples 3 and 4.

The basic formulation was:

	Parts by weight
Rubber solids (from natural rubber latex)	100
Sulfur	3
Accelerator	1
Titanium oxide	5
Zinc oxide	3

In each example the foregoing compounding ingredients, together with the anti-oxidant or pinking inhibitor, or both, were commingled with natural rubber latex, the resulting mixture was then coagulated as a thread in the conventional way and the resulting thread was cured in conventional manner.

Example 1

There was included in the above formulation one part of symmetrical di-beta-naphthyl-para-phenylene diamine. The resulting thread upon subjection to an accelerated pinking test (in the Weatherometer but with the samples facing away from the carbon arc) began to pink after 15 minutes and after one hour was a very pronounced

red. The unaged material had a tensile strength of 6000 p. s. i. and an elongation of 715%. After aging 400 hours in the Bierer-Davis oxygen bomb it showed a tensile strength of 3550 p. s. i. and an elongation of 600%.

Example 2

With the basic formulation given above there was included one and two parts (in two tests) of 2,5-di-tertiary butyl hydroquinone. The unaged vulcanizates had a tensile of 5750 p. s. i. and an elongation of 690%. Upon aging 400 hours in the same manner as in Example 1 the vulcanizates were completely disintegrated and worthless.

Example 3

With the basic formulation there was included one part of symmetrical di-beta-naphthyl-paraphenylene diamine and two parts of 2,5-di-tertiary butyl hydroquinone. The aging properties of the vulcanizate were equal to those of the vulcanizate of Example 1. The material was subjected to accelerated pinking exactly as in Example 1. Pinking did not begin until 100 minutes had elapsed.

Example 3 clearly indicates that the employment of two parts of 2,5-di-tertiary butyl hydroquinone is highly effective in inhibiting pinking when one part of the anti-oxidant in question is employed. The inhibiting of pinking effected by use of two parts of 2,5-di-tertiary butyl hydroquinone in accordance with this example is sufficient to eliminate pinking under ordinary conditions.

Example 4

Example 3 is duplicated exactly except that four parts of 2,5-di-tertiary butyl hydroquinone are employed. When the resulting material was subjected to the standard pinking test as before, it did not begin to pink until 220 minutes had elapsed.

The inhibition of pinking effected by the use of four parts of inhibitor in accordance with Example 4 is sufficient to eliminate pinking even under the most severe conditions encountered in practice.

The amount of symmetrical di-beta-naphthyl-paraphenylene diamine employed may vary widely. However, it will usually range from 0.25 to 2.0% by weight based on the rubber. In any event, the amount should be sufficient to be effective as an anti-oxidant for the vulcanizate.

The amount of 2,5-di-tertiary butyl hydroquinone may vary widely. The inhibiting effect is roughly proportional to the amount employed. The amount used will depend upon the extent of inhibition desired and upon the conditions to which the vulcanizate is subjected.

Generally speaking the amount of 2,5-di-tertiary butyl hydroquinone will range from 0.25 to 5% by weight based on the rubber. I prefer to employ 2% by weight of the inhibitor based on the rubber as giving practically complete protection against pinking under field conditions.

The pinking inhibitor of the present invention confers the additional benefit that it markedly decreases discoloration of the vulcanizate upon exposure to light. Such discoloration is to be distinguished from pinking. As is well known, symmetrical di-beta-naphthyl-paraphenylene diamine turns gray upon exposure to light. For example, a vulcanizate of the regular production type made with one part of this anti-oxidant per 100 parts of rubber turns dark gray in color upon direct exposure for two hours to the carbon arc of the Weatherometer. In contrast, the product of Example 3 which contains two parts of the inhibitor turns only a medium gray upon the same exposure while the product of Example 4 turns only a very light gray upon the same exposure.

The use of the inhibitor of my invention is without any disadvantages. It does not adversely affect the properties of the vulcanizate in any respect. Its advantages are great. The principal advantage, of course, is that it prevents the pinking due to the anti-oxidant. As just mentioned it has the additional advantage of greatly reducing light discoloration.

My invention can be applied to any rubber stock in which symmetrical di-beta-naphthyl-paraphenylene diamine is used as an anti-oxidant, including stocks wherein the rubber is natural rubber, or synthetic rubber such as rubbery copolymers of butadiene and styrene, neoprene, etc. The invention is generally applied to natural rubber stocks.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. A sulfur-vulcanized rubber article containing a small amount of symmetrical di-beta-naphthyl-para-phenylene diamine incorporated before vulcanization and effective to protect the vulcanized rubber against oxidation, the formulation of said vulcanized rubber article being such that in the absence of the hereinafter specified 2,5-di-tertiary butyl hydroquinone it would exhibit an objectionable tendency to develop a visible pink discoloration by reason of the presence of said diamine, said vulcanized rubber article being protected against said tendency to develop said visible pink discoloration by the presence therein of a small amount of 2,5-di-tertiary butyl hydroquinone incorporated before vulcanization.

2. A sulfur-vulcanized rubber article containing from 0.25 to 2.0% by weight based on the rubber of symmetrical di-beta-naphthyl-paraphenylene diamine incorporated before vulcanization and effective to protect the vulcanized rubber against oxidation, the formulation of said vulcanized rubber article being such that in the absence of the hereinafter specified 2,5-di-tertiary butyl hydroquinone it would exhibit an objectionable tendency to develop a visible pink discoloration by reason of the presence of said diamine, said vulcanized rubber article being protected against said tendency to develop said visible pink discoloration by the presence therein of from 0.25 to 5.0% by weight based on the rubber of 2,5-di-tertiary butyl hydroquinone incorporated before vulcanization.

3. A sulfur-vulcanized rubber article containing approximately 1% by weight based on the rubber of symmetrical di-beta-naththyl-paraphenylene diamine incorporated before vulcanization and effective to protect the vulcanized rubber against oxidation, the formulation of said vulcanized rubber article being such that in the absence of the hereinafter specified 2,5-di-tertiary butyl hydroquinone it would exhibit an objectionable tendency to develop a visible pink discoloration by reason of the presence of said diamine, said vulcanized rubber article being protected against said tendency to develop said visible pink discoloration by the presence therein of approximately 2% by weight based on the rubber of 2,5-di-tertiary butyl hydroquinone incorporated before vulcanization.

4. Elastic yarn having a core of sulfur-vulcan-

ized rubber under tension and having a wound covering of textile yarn, said vulcanized rubber containing a small amount of symmetrical di-beta-naphthyl-para-phenylene diamine incorporated before vulcanization and effective to protect the vulcanized rubber against oxidation, the formulation of said vulcanized rubber being such that in the absence of the hereinafter specified 2,5-di-tertiary butyl hydroquinone it would exhibit an objectionable tendency to develop a visible pink discoloration by reason of the presence of said diamine, said vulcanized rubber being protected against said tendency to develop said visible pink discoloration by the presence therein of a small amount of 2,5-di-tertiary butyl hydroquinone incorporated before vulcanization.

5. A vulcanizable composition containing rubber, sulfur as a vulcanizing agent therefor, and a small amount of symmetrical di-beta-naphthyl-para-phenylene diamine effective to protect the rubber after vulcanization against oxidation, the formulation of said composition being such that in the absence of the hereinafter specified 2,5-di-tertiary butyl hydroquinone the vulcanizate of said composition would exhibit an objectionable tendency to develop a visible pink discoloration by reason of the presence of said diamine, said composition being protected against said tendency to develop said visible pink discoloration by the presence therein of a small amount of 2,5-di-tertiary butyl hydroquinone.

6. In the manufacture of a sulfur-vulcanized rubber article containing a small amount of symmetrical di-beta-naphthyl-para-phenylene diamine effective to protect the vulcanized rubber article against oxidation, said article being so formulated that in the absence of the hereinafter specified 2,5-di-tertiary butyl hydroquinone it would exhibit an objectionable tendency to develop a visible pink discoloration by reason of the presence of said diamine, the improvement which comprises preventing development of said visible pink discoloration in the vulcanizate of said composition by incorporating in the formulation prior to vulcanization a small amount of 2,5-di-tertiary butyl hydroquinone.

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